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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Michael Wen-Chein Yang, et al.

Serial No.: **09/921,589**

Group Art Unit: **1752**

Filing Date: **August 3, 2001**

Examiner: **Cynthia Hamilton**

For: **LASER IMAGED PRINTING PLATES**

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DECLARATION OF EDWARD T. MURPHY

I, Edward T. Murphy, hereby declare that:

1) I have over 12 years of experience in managing the development of printing plates, including considerable background in the area of laser imaged printing plates containing a photopolymerizable layer and an ablatable layer.

2) I received a Bachelor of Arts degree in Mechanical Engineering from the Western New England College in 1971, and engaged in graduate studies in Mechanical Engineering at the University of Massachusetts from 1971 to 1975. I am registered as a Professional Engineer with the Commonwealth of Massachusetts.

3) From 1969 to 1973, I was employed by the Scott Graphics Company as a Process Development Engineer. During this time I performed research in coatings processes as they related to high resolution graphics imaging products.

4) From 1973 to 1994, I was employed by the W.R. Grace Company. During this time I held numerous positions including Process Engineer, Plant Manager, Manufacturing Manager

and Director of Engineering for the company's Polyfibron Division. From 1988 to 1994, I held the position of General Manager of Printing Plates for North America. In this position, I oversaw the business unit's research activities and, in fact, personnel involved in research and development of printing plates reported to me.

5) In 1994, W.R. Grace spun off the Polyfibron Division as Polyfibron Technologies, Inc., and I continued as General Manager of Printing Plates for North America at Polyfibron until 1999. MacDermid Graphic Arts acquired Polyfibron in December, 1999. I continued in my position as General Manager at MacDermid until I left the company in December, 2000.

6) Since December, 2000 I have become the President of GES Corporation. In this position, I am involved in the development, manufacturing, and marketing of physical therapy devices.

7) I have reviewed the patent application entitled "Laser Imaged Printing Plates" (copy attached as Exhibit A) which I understand to have been filed with the United States Patent and Trademark Office on June 25, 1993. I have also reviewed a set of patent claims (*i.e.*, claims 10 to 14, 17 and 18, copy attached as Exhibit B) that I understand to be pending in application Serial No. 09/921,589.

8) I understand that the Patent Office has asserted that claims 10 to 14, 17 and 18 contain subject matter that was not described in the June, 1993 patent application in such a way as to reasonably convey to those skilled in the art that the inventors had possession of the claimed subject matter.

9) I do not agree with the Patent Office that the subject matter defined by claims 10 to 14, 17 and 18 is not described in the June, 1993 patent application. It was apparent to me, upon review of the patent application, that it described the claimed subject matter, and that its inventors invented (and thus had possession of) this subject matter.

10) I consider myself to be a person having skill in the field to which the claimed photosensitive elements pertain, and also to be a person who had skill in this field in 1993. Each of claims 10 to 14, 17 and 18 is directed to photosensitive elements that contain a backing layer, a layer of photopolymerizable material, and an ablatable layer. The ablatable layer includes at least one infrared absorbing material and at least one binder. As indicated in the foregoing summary of my education and work experience, I have been involved in this filed since about 1988.

11) The patent application that is attached as Exhibit A describes photosensitive elements that contain a layer that is ablatable by laser radiation. The patent application does not require that a particular wavelength of laser radiation, or range of wavelengths, be used and, in fact, repeatedly refers to ablation at a "selected wavelength" or at an "appropriate wavelength" (see, for example, page 8, line 13; page 9, lines 23-24; page 10, line 34 to page 11, line 1; page 12, line 15 and lines 19-20; and page 13, lines 5-6). Consistent with this teaching, the patent application indicates at, for example, page 14, lines 18 to 20, that the wavelength of the laser used for ablation must be such that the laser treatment ablates the ablatable layer without damaging the photoplymer layer to an extent that it cannot subsequently be used as a printing surface.

12) In this regard, the patent application also describes experiments (in particular, Examples 3 to 7) in which ablation layers of photosensitive elements were ablated using IR laser radiation or UV laser radiation. Although the specification does not require that ablation occur at any particular wavelength, these experiments indicate to me that the use of IR lasers, as well as UV lasers, is preferred. For example, Example 3 describes ablation using a laser operating at a wavelength in the infrared region, *i.e.*, 10.6 μm, and describes tests conducted using a laser at other infrared wavelengths, *i.e.*, 1.06 μm. Although the YAG

laser in Example 3 was not effective in causing ablation under the particular operating conditions employed, those skilled in the art would have understood that the absence of ablation resulted from operating the laser at the relatively low power level that was being tested in Example 3, and that this could easily be remedied by operating the laser at a higher power level. Table II, for example, demonstrates that a CO_2 laser emitting in the infrared region was effective in causing ablation at some intensity levels, but was ineffective in causing ablation of the layers when operating at others. Those skilled in the art, therefore, would have understood that a YAG laser (also emitting in the infrared region) would be effective in causing ablation of the ablation layer if simply operated at, for example, a greater intensity level.

13) The 1993 patent application does not require that a particular binder must be present in the layer of the photosensitive element that is ablatable by laser radiation. The application lists numerous examples of binders that can be used in the ablation layer, including polyacetal, polyacrylic, polyamide, polyimide, polybutylene, polycarbonate, polyester, polyethylene, cellulosic polymer, polyphenylene ether, and polyethylene oxide binders, and indicates that cellulosic and polyamide binders are preferred (see page 11, line 32 to page 12, line 3). The disclosure provided in the 1993 patent application indicates to me that any of the listed binders can be used in the ablation layer .

14) The 1993 patent application also describes photosensitive elements whose ablatable layers include a material that provides opacity to the wavelength of light that is used to cure photopolymerizable material in the element. The patent application, for example, states that "UV flood lamps normally provide the light for curing" (page 11, lines 26-27), and indicates that the presence of a UV absorber in the ablatable layer imparts UV opacity to the layer

(page 9, lines 31 to 33). The patent application further states that the spectral range of the flood-exposure lamps used "in *most* applications" is 300-400 nm, that the UV absorber "*typically* should be active in this range," and that an alternative way of stating this is to say that the UV absorber must have a high extinction coefficient "in the *spectral output range of the developer lamps*" (page 10, lines 5 to 11, emphasis added). A "UV absorber," as described in the specification, is a material that absorbs the radiation used during the curing process, rendering the ablation layer opaque to such radiation. A material would be considered to be a "UV absorber" according to the 1993 patent application so long as it absorbs UV radiation, whether or not it also happens to absorb IR radiation. Thus, a material used as a UV absorber in the ablatable layer that is described in the application could be active in the IR range, and could absorb both UV and IR radiation.

15) I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

10/21/02 Edward V. Murphy

Date Edward T. Murphy

EXHIBIT A

Ref. 01-8480

LASER IMAGED PRINTING PLATE

Inventors: Michael W. Yang
Rustom S. Kanga
Alvin V. Randall

Field of the Invention

This invention relates to printing plates which can be made without using a negative. More specifically, it relates to a laser-imageable printing plate. Such plates are particularly useful for flexographic printing, but can be used for offset and lithographic printing.

Background of the Invention

Flexography is a method of printing that is commonly used for high-volume runs. Flexography is employed for printing on a variety of substrates such as paper, paperboard stock, corrugated board, films, foils and laminates. Newspapers and grocery bags are prominent examples. Coarse surfaces and stretch films can be economically printed only by means of flexography. Flexographic printing plates are relief plates with image elements raised above open areas. One type of flexographic printing plate resembles a transparent or translucent plastic doormat when it is ready for use. The plate is somewhat soft, and flexible enough to wrap around a printing cylinder, and durable enough to print over a million copies.

Such plates offer a number of advantages to the printer, based chiefly on their durability and the ease with which they can be made. Further improvements, to the degree of resolution (fineness of detail) which can be obtained as well as reductions in cost, would expand the usefulness of these plates. The present invention allows both increased resolution by use of laser processing, and reductions in cost

through the elimination of the use of a negativ to make the printing plate.

A typical flexographic printing plate as delivered by its manufacturer is a multilayered article made of a backing, an unexposed photocurable layer, a protective layer or slip film, and a cover sheet. The backing lends support to the plate. It is typically a plastic sheet about 5 mils or so thick, which may be transparent or opaque. The photocurable layer may be anywhere from about 25-275 mils thick, and can be formulated from any of a wide variety of known photopolymers, initiators, reactive diluents, fillers, etc. The slip film is a thin (about 0.1 - 1.0 mils) sheet which is transparent to UV light that protects the photopolymer from dust and increases its ease of handling. The cover sheet is a heavy, protective layer, typically polyester, plastic or paper.

In normal use, the printer will peel the cover sheet off the printing plate, and place a negative on top of the slip film. The plate and negative will then be subjected to flood-exposure by UV light through the negative. The areas exposed to the light cure, or harden, and the unexposed areas are removed (developed). Typical methods of development include washing with various solvents or water, often with a brush. Other possibilities for development include use of an air knife or heat plus a blotter.

Exposure of the printing plate is usually carried out by application of a vacuum to ensure good contact between the negative and the plate. Any air gap will cause deterioration of the image. Similarly, any foreign material, such as dirt and dust between the

negative and the plate results in loss of image quality.

Even though the slip films are thin and made from transparent materials, they still cause some light scattering and do somewhat limit the resolution which can be obtained from a given image. If the slip film were eliminated, finer and more intricate images could be obtained.

Finer resolution would be particularly desirable for the reproduction of elaborate writing as in the case of Japanese characters, and for photographic images.

A negative can be a costly expense item. For one thing, any negative which is used for printing must be perfect. Any minor flaw will be carried through onto each printed item. As a consequence, effort must be expended to ensure that the negative is precisely made. In addition, the negative is usually made with silver halide compounds which are costly and which are also the source of environmental concerns upon disposal.

Given these considerations, it is clear that any process which would eliminate the use of the negative, or reduce the light scattering effects and other exposure limitations of the slip films, would yield significant advantages in terms of cost, environmental impact, convenience, and image quality over the present methods.

The inventors have found a way to obtain these advantages by using a laser guided by an image stored in an electronic data file to create an *in situ* negative on a modified slip film, and then exposing and developing the printing plate in the usual manner. As a result, the printer need not rely on the use of

negatives and all their supporting quipment, and can rely inst ad on a scanned and stored image. Such im~ges can be readily altered for different purposes, thus adding to the printer's convenience and flexibility. In addition, this method is compatible with the current developing and printing equipment, so expensive alterations to the other equipment are not required.

Laser engraving of various materials, such as wood and metal, is well known. Laser engraving of cured hard rubber or lithographic plates is also known. If this procedure were applied to a flexographic printing plate, the plate would first be exposed to UV light without an image. Then the laser would be used to engrave an image on the hardened plate. This has been attempted, but found to be too slow to be commercially competitive. Flexographic printing plates require a high relief (30-40 mil high letters) which take a long time to engrave.

Direct exposure of a photopolymer using a laser is also known. This procedure use a precisely guided laser to replace the UV flood lamps which are normally used to expose the plate. United States Patent 4,248,959, issued to Jeffers et al. February 3, 1981, relates to the direct exposure of a photosensitive polymer plate using a laser guided by a computer-generated image. The disclosed method is not suitable for the development of flexographic printing plates, again because the thickness of the plate hampers the cure. Again, the process is too slow to be commercially competitive.

Other efforts have focussed on generating an image directly in contact with a photocurable layer. United States Patent 5,015,553 issued to Grandmont et

al. May 14, 1991 relates to a method of making a UV photoresist for a printed circuit board, using a computer-assisted design (CAD) driven photoplotter which selectively exposes a photographic imaging layer without affecting the underlying UV sensitive photoresist. The image layer is then chemically developed on the board and used as an situ mask for the underlying UV resist during exposure to UV light. After the exposure, the image layer is peeled off to allow conventional processing of the resist. The process requires at least two development steps for the entire plate, and also requires the use of a peelable cover sheet interposed between the image layer and the photocurable layer.

Laser ablation of polymers from relatively insensitive substrates is known. United States Patent 4,020,762 issued to Peterson May 3, 1977 relates to a method of making a sensitized aluminum printing plate for offset lithography. An aluminum sheet was coated with a mixture of finely divided carbon, nitro-cellulose, a non-oxidizing alkyd resin, a diazo sensitizer, cellulose acetate, butylacetate, xylene and ethyl cellosolve. The coating was at least partially etched with a YAG laser. It is not clear whether all the coating was removed from the aluminum substrate although the text alludes to this result. The patentee discloses that the etched areas became sensitive to UV light, and that the etched areas, after exposure to UV light and development, accepted ink, while the areas which were not etched accepted water. No quantitative results are presented. There is no indication that the liquid coating in the reference would be usable as a flexographic printing plate. Ther- is no indication that the laser ablation

was precise enough to allow removal of a polymer layer to uncover a photosensitive polymer lay r directly beneath.

Lasers have also been used to physically transfer small amounts of polymer from one layer of a multilayer article to another. United States Patent 5,156,938 issued to Foley et al. October 30, 1992, relates to a method of laser-induced ablative transfer imaging suitable for the production of masks (negatives) for the graphic arts and printed circuit industries. In this process, a laser-sensitive material is physically displaced from a donor layer of a multilayer structure to a receptor layer.

This is described as an ablative transfer because some of the materials from the donor layer are ablated while other materials are deposited on the receptor layer.

The inventors have discovered that if a slip film, of the type already in use with flexographic plates, is modified with a strong UV absorber, a laser can be used to engrave the slip film instead of the photopolymer. The slip film, then, effectively becomes a negative that is created *in situ*. There is no need to separately manufacture a negative, or to eventually dispose of silver halide. Also, the light scattering effects of the slip film are eliminated, thereby increasing resolution of the image.

Objects of the Invention

It is therefore an object of the present invention to provide a method of making a printing plate which does not require the use of a photographic negative.

Another object of this inv ntion is to make a laser-imageable printing plat .

Yet another object of this invention is to provide a protective layer for a photocurable article that can be conveniently and accurately removed by laser ablation from the article.

The objects of this invention can be accomplished by providing a protective layer for a photocurable article comprising

- o a polymeric matrix and
- o a dopant having a high extinction coefficient in the range of 300-400 nm, the layer responding to a threshold dosage of radiation at a selected wavelength by photoablation of the polymeric matrix and, preferably, photobleaching of the dopant. The layer is applied to a photosensitive article, and then a laser is employed to selectively remove the protective layer, exposing the photocurable composition underneath to subsequent exposure to UV light and cure. The cured plate then can be developed in the normal fashion.

Other objects and advantages of this invention will become apparent through the disclosure herein.

Detailed Description of the Invention

The Exposure and Development Process

The present invention includes a method of making a laser imaged printing plate. First, a solid, uncured printing plate is modified with a UV absorber. This is most conveniently done by adding a UV absorber to the normally UV transparent slip film which is already adapted for use with the printing plate, and applying the sam in the usual fashion to the surface

of the uncured printing plate. Th printing plate with the modifi d slip film can be stored for a time, or used immediately, as the printer's needs dictate.

When the printing plate is to be used, a laser is employed to selectively ablate, or remove, the slip film. The uncured plate is then flood-exposed to UV light in the usual fashion. The areas where the slip film was ablated will cure, or harden, upon exposure to the UV light. The areas where the slip film was not ablated will remain uncured. The uncured areas can then be washed away in the normal development process.

This application is written in terms of the specific embodiment in which the invention was first applied, that is, flexographic printing plates. One of ordinary skill in the art will readily recognize that this invention is not limited to this embodiment. For example, in this invention the slip film is used as a carrier for the UV absorber. This is a matter of convenience, as the slip film was already available in the existing plates for use. Similarly, a UV transparent film which has been doped with a UV absorber and ablated by a laser operating at a selected wavelength could be used as the printing sleeve for gravure printing, or as an in situ mask for making photoresists.

The UV Absorber

One important aspect of the present invention is that the slip film, which would normally be transparent to UV light in order to facilitate the imaging process, is modified with a UV absorber. The presence of the UV absorber makes a normally UV transparent slip film into highly UV opaque barrier.

It is critical that the UV absorption be nearly complete, at least 97%, preferably mor than 99.9%, and even more preferably 99.99%, so that substantially all the radiation from the UV flood-exposure lamps will be blocked. The spectral range of the flood-exposure lamps used in most applications is 300-400 nm. Therefore the UV absorber typically should be active in this range. An alternative way of stating this is to say that the UV absorber must have a high extinction coefficient in the spectral output range of the developer lamps.

Benzophenone derivatives and strongly absorbing dyes are favored. The following materials have high extinction coefficients within the typical spectral range of developer lamps:

Uvinul D 49™	(2,2'-dihydroxy-4,4'-dimethoxy-benzophenone) available from BASF Corp., Parsipanny, NJ;
Uvinul D 50™	(2,2',4,4'-tetrahydroxybenzophenone) available from BASF Corp., Parsipanny, NJ;
Uvinul N 539	(benzophenone cyanoacrylate) available from BASF Corp., Parsipanny, NJ;
4-(dimethylaminobenzophenone)	available from Aldrich Chemical Company, Milwaukee, WI;
Tinuvin P™	(benzotriazole) available from Ciba-Geigy Corp., Hawthorne, NY;
Intrawite OB™	A dye Available from Crompton & Knowles Ltd, Reading, PA;
Intraplast Yellow 2GLN,	a dye available from Crompton & Knowles;
4-phenylazophenol ("4-PAP")	available from Aldrich.

The UV absorber must also exhibit a specific response to excitation by laser at an appropriate

wavelength: It must allow the ablation of the slip film. Finally, the UV absorb r must be compatible with the slip film, and not exhibit significant migration from the slip film to the photocurable composition.

Preferred UV-absorbers which have been found to have these characteristics are Uvinul™ D 49 and D 50 (BASF) and 4-phenylazophenol. These materials cause photoablation of a typical slip film upon exposure to a threshold power level (fluence) at the selected wavelength of 351 nm. In addition, they have the added advantage of photobleaching at 351 nm. The UV absorber is typically present in the film in amounts of about 1-20 PHR (parts per hundred, or 1/101-20/120 percent); preferably about 4-8 PHR when the slip film is 0.1 to 1.0 mils, preferably 0.3 to 0.5 mils.

The Slip Film

As discussed above, the preferred vehicle for the UV absorber in some embodiments of the present invention is the slip film, a thin, protective film used with a printing plate which is to be imaged. These films are made of a wide variety of polymers which are compatible with the underlying photopolymer and easily removed during the development (wash) step. When a negative is used, the slip film has to be transparent to the light used for curing. Since UV flood lamps normally provide the light for curing, the normal slip film is transparent in the range of 300-400 nm. Such films are well known in the photoprocessing field, and in principle, any such film may be modified by adding the UV absorber of the present invention. Examples include polyacetals, polyacrylics, polyamides, polyimides, polybutylenes,

polycarbonates, polyesters, polyethylenes, cellulosic polymers, polyphenylene ethers, and polyethylene oxides. Cellulosics and polyamides are preferred. The addition of the UV absorber may change the film's response to the laser used in the present invention. For example, many films are not normally affected by exposure to laser radiation at 351 nm, but when Uvinul D 50 is added, these films become vulnerable to laser ablation, and useful in the present process.

The Photocurable Composition

In principle, any of the known photocurable formulations can be used in the present invention. However, it is particularly helpful if the type of photopolymer and initiator used are compatible with the laser or the wavelength selected for use in the process.

Photopolymer

Of the photopolymers, those which are unaffected by laser radiation at the particular wavelength selected for the practice of the present invention are particularly useful. Of these, polyurethanes, including acrylate polyurethanes, acid-modified acrylate polyurethanes, amine-modified polyurethanes, rubbers, including acrylonitrile rubbers, and di- and triblock copolymers such as those made from styrene-isoprene and styrene-butadiene may be mentioned. The amine-modified acrylate polyurethanes and styrene-isoprene or styrene-butadiene di- and triblock copolymers are preferred. An uncured printing plate made from such a photopolymer can withstand some exposure to the laser energy without incurring thermal damage. Thus the photopolymer and various additives

exc pt the initiator should have a low absorbance at the laser's operating wavelength.

Initiator

The initiator can also have a low absorbance at the wavelength of the laser selected for use in the present invention. However, if the initiator is activated in response to the selected wavelength, cure of the photopolymer will begin during the ablation step, without damage to the photopolymer, before flood-exposure by the UV lamps. Use of the appropriate initiator can, therefore, speed processing of the plate and help insure a faster, more uniform cure.

Photoinitiators for the photocurable composition include the benzoin alkyl ethers, such as benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether and benzoin isobutyl ether. Another class of photoinitiators are the dialkoxyacetophenones exemplified by 2,2-dimethoxy-2-phenylacetophenone, i.e., Irgacure® 651 (available from Ciba-Geigy, Hawthorne, NY); and 2,2-diethoxy-2-phenylacetophenone. Still another class of photoinitiators are the aldehyde and ketone carbonyl compounds having at least one aromatic nucleus attached directly to the carboxyl group. These photoinitiators include, but are not limited to, benzophenone, acetophenone, o-methoxybenzophenone, acenaphthenequinone, methyl ethyl ketone, valerophenone, hexanophenone, alpha-phenylbutyrophenone, p-morpholinopropiophenone, dibenzosuberone, 4-morpholinobenzophenone,4'-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone, 4'-methoxyacetophenone, benzaldehyd , alpha-tetralone, 9-acetylphenanthrene,

2-acetylphenanthrene, 10-thioxanth none, 3-ac tylphenanthrene, 3-ac tylindone, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, xanthene-9-one, 7-H-benz[de]-anthracene-7-one, 1-naphthaldehyde, 4,4'-bis(dimethylamino)-benzophenone, fluorene-9-one, 1'-acetonaphthone, 2'-acetonaphthone, 2,3-butanedione, acetonaphthene, benz[a]anthracene 7.12 dione, etc. Phosphines such as triphenylphosphine and tri-o-tolylphosphine are also operable herein as photoinitiators.

Benzophenone-based initiators are preferred. An example that is commercially available is Irgacure 651.

<u>The Laser</u>

A laser is employed to precisely remove the slip film exposing the photopolymer underneath to subsequent flood exposure and cure. The wavelength and power of the laser should be such that the laser treatment can ablate the slip film without damage to the photopolymer layer just beneath. Excimer lasers which operate in a pulse mode having a wavelength of 350 ± 50 nm, preferably about 351 nm are usable. The preferred dosage level is 1-5 Joules per cm^2 (J/cm^2).

The following examples illustrate the present invention without limiting it, or the claims which follow.

<u>Example 1</u>

Preparation of Uvinul D 50 Modified Polyamide <u>Slip Film For KOR Flexographic Plates</u>

In this example, the slip film which would normally be used with a commercially available flexographic printing plate is modified by the addition of a UV absorber so that zero transmittance

(as demonstrated by protection from cure upon exposure to UV flood lamps) is achi ved.

A stock casting solution was prepared with the following formulation:

Isopropanol	45.6 parts
Hexane	23.9 parts
VM&P Naphtha[1]	21.6 parts
Macromelt 6900™[2]	8.3 parts
Uvinul D 50	0.664 parts

Footnotes:

1 Aromatic solvent mixture available from Ashland Chemical Co., Columbus, OH

2 Polymer pellets available from Henkel Corp., Lagrange, IL

Films approximately 5 to 7 mils thick were hand cast on a clear Mylar™ backing sheet using a drawdown bar. Upon drying, the average film thickness was measured using a Ono Sokki micrometer to be around 0.3-0.5 mils.

The films were laminated onto a commercially available photopolymer composition to make a UV absorber-modified printing plate analagous to the KOR® printing plate available from W. R. Grace & Co.-Conn., Atlanta, Ga. The plates were exposed through a test negative using commercially available UV flood lamps. Three different concentrations (4 PHR, 6 PHR and 8 PHR based on percent solids), three levels of thicknesses (low, medium and high) and two exposure levels were employed for the study which is summarized in Table I. Presence or absence of an image was an indication of the effectiveness of the UV absorber for blocking the incident UV radiation. For the 4 and 6 PHR loadings, an image was seen when the slip thickness was less than 0.4 mils, indicating a lower threshold concentration of D 50 to effectively block all UV light. For 8 PHR loadings, 0.3-0.4 mils was seen to

be sufficient to block all UV light as seen by an absence of an image. For all three concentrations, a thickness above 0.5-0.6 mils was effective.

The modified slip film was then laminated onto a Flex Light KOR® ("KOR") plate which was approximately 25 to 275 mils thick. The laminated plates were annealed at 75° F, and used for laser ablation trials, as shown in Examples 3-6.

TABLE I
Studies on the Concentration of Uvinul D 50
Versus Thickness of the Slip Film

	Thickness		Exposure	
Concentration[1]	Wet (mils)	Dry (mils)	3½ min.	7 min.
4 PHR	7	0.1-0.2	I[2]	I
4 PHR	10	0.2-0.3	I	I
4 PHR	15	1.4-1.5	N[3]	N
6 PHR	7	0.2-0.3	I	I
6 PHR	10	0.4-0.5	N	N
6 PHR	15	0.7-0.8	N	N
8 PHR	7	0.3-0.4	N	N
8 PHR	10	0.4-0.5	N	N

Footnotes:

1 - Per hundred based on percent solids.
2 - I: Formation of image. D 50 not effective in blocking UV light.
3 - N: No image. D 50 effective.

Example 2

Preparation of Uvinul D 50 Modified Cellulosic-Based Water-Wash Slip Film for Amino-Modified Polyurethane (AMPU) Aqueous-Developable Flexographic Plates

In this Example, another type of slip film, a cellulose film adapted for use with a water-washable flexographic printing plate, is modified with a UV absorber. The concentration and thickness found in the previous Example were utilized to ensure the maximum UV absorption by the film.

A stock solution was prepared using the following formulation:

Isopropanol	50.2 parts
Water	39.8 parts
Klucel L[1]	10.0 parts
Uvinul D 50	0.8 parts

Footnote:

[1] Hydroxypropyl cellulose polymer pellets available from Aqualon, Inc., Wilmington, DE

As before, films 5 to 7 mils thick were cast on a clear Mylar™ backing sheet, dried and laminated onto a developmental amine-modified polyurethane flexo substrate. The plates were between 25 mils and 275 mils thick. Laser ablation and imaging was carried out on the modified plates as shown in Examples 3-6.

Example 3

Laser Ablation and Imaging Using a Solid-State Sealed CO_2 Laser (10.6 nm)

The commercially available photopolymer resin of Example 1 was formed into a sheet and laminated with 0.9 mil thick polyamide slip film containing 8 PHR

Uvinul D 50 to make an experimental printing plate (KOR). The plat s for this preliminary study were prepared using a hand cast slip film. Two different laser systems were employed for the ablative studies: a sealed-CO_2 absorbing at 10.6 μm and a YAG at 1.06 μm. The YAG laser was found to be essentially ineffective in causing any ablation. The power in the sealed-CO_2 laser was varied from 8 watts to a high of 15 watts. Digital image programming allowed ablation of a rectangular profile (1 cm x 2 cm) and also lettering. Results from the ablative studies are summarized in Table II.

The presence or absence of the polyamide slip film was investigated by ATR-IR analysis. The ablated plate was then flood exposed with hot lamps for 6 minutes and developed in Solvit®, the usual development solvent for commercial purposes available from Polyfibron Division of W. R. Grace & Co.-Conn., Atlanta, GA, for 6 minutes. From Table II it is seen that the etch depth versus fluence (power) was not linear. The difference in etch depth between 8 to 10 Watts is barely more than the experimental error of 0.1 mils. At 12 Watts, the 0.5 mil slip film had been complete ablated, along with some of the underlying photopolymer. There was also a jump in the etch depth from 0.7 mils to 5.0 mils when the power is increased from 12 watts to 15 watts. As expected, only those rectangular profiles which show almost complete ablation of the slip film cured during subsequent flood exposure and development. However, even for those profiles, the surface was highly textured and

TABLE II

CO_2 Laser-Ablative Imaging Studies on Uvinul D 50
Modified Slip Film Laminated on KOR

			Plate Imaging		
#	Power Watts	Etch Depth mils	Rectangular Profile	Lettering	Comments
2	8	-	Washed away	Washed away	Not enough ablation
5	9	0.1-0.3	Washed away	Washed away	Not enough ablation
6	10	0.3-0.4	Washed away	Washed away	Not enough ablation
8	12	0.7	Cured, 68 mils	Washed away	Plate surface uneven
12	15	5.0	Cured, 64 mils	Cured	Plate surface uneven

rough. Also, the resolution was poor for the letters. Thus, it was seen that the basic idea of the laser-imaged printing plate was demonstrated, and that use of the CO_2 laser resulted in thermal ablation with a consequent loss of resolution.

Example 4

Laser ablation and imaging using Krypton Fluoride (KrF) Excimer Laser at 248 nm

The experimental printing plates made according to Example 1 (KOR) and 2 (AMPU) above were imaged as in Example 3 using a krypton fluoride excimer laser controlled by digital imaging programming. The results are summariz d in Table III.

The krypton fluoride excimer laser at 248 nm was found to be extremely effective in causing photoablation. Since most polymers including the polyamide of the slip film and the Kraton™ rubber of the photopolymer of Example 1 have very strong absorption at 248 nm, even small fluences (<0.5 J/cm^2) caused ablation of the slip. The mechanism is believed to be mainly photoablation (i.e., chemical bond-breaking of the polyamide) and some thermal ablation due to heat generation. Unfortunately, since the styrene-isoprene rubber used to make the photopolymer is also very strongly absorbing at this wavelength, some damage to the surface occurred, especially at higher fluences. Where thermal damage occurred, resolution was poor.

TABLE III

Laser Ablation of KOR and AMPU Using
KrF Excimer Laser (248 nm)

Type	Fluence J/cm^2	# of Pulses	Image	Comments
KOR (Ex.1)	0.4	10	Yes	Thermal Damage. Poor resolution for all.
		40	Yes	
		70	Yes	
	1.2	1	No	
		2	No	
		6	Yes	Swell due to incomplete cure. Poor resolution.
		8	Yes	
AMPU (Ex.2)	0.4	10	Yes	Thermal Damage. Poor resolution
		40	Yes	
		20	Yes	
	1.2	1	No	Incomplete Ablation
		2	No	Incomplete Ablation
		6	Yes-	Thermal Damage. Poor resolution
		8	Yes	

Example 5

Optimization of Fluences for 351 nm Xenon Fluoride (XeF) Excimer Laser

Laser ablation and imaging studies and optimization of fluences necessary for ablation was carried out as before on KOR (Ex. 1) and AMPU (Ex. 2). Similar results were seen for both types of plates. The consolidated results are summarized in Table IV.

Most polymers do not absorb at 351 nm. However, the modified slip films (both the solvent-based polyamide and the aqueous-based cellulosic polymers) were very sensitive to the excimer laser at 351 nm due to the high extinction coefficient of D 50 at this wavelength. A combination of photobleaching (destruction of D 50 molecules) and photoablative (transfer of the energy absorbed by D 50 to the polymer causing bond breaking in the polymer) effects were seen.

The modified slip is partially ablated at lower doses (<1 J/cm^2) resulting in either no cure (and hence no image) or incomplete cure (and hence poor image and resolution). A complete ablation was seen at higher doses (>1.5 J/cm^2). There was no damage to the plate surface. Subsequent flood exposure and development gave a very sharp image of the ablated area with good resolution.

TABLE IV

Optimization of Fluences for Laser Imaging Using Xenon-Fluoride Excimer Laser at 351 nm for KOR and AMPU

Fluence J/cm^2	# of Pulses	Image	Comments
0.14	50 100 200	No No No	Fluence was below the threshold and hence incomplete ablation
0.4	5 10 15 30	No No No No	Below threshold fluence. Did not cure.
0.9	1 2 6 10	No No Yes Yes	Not enough ablation. Not enough ablation. Incomplete cure, image swelled in solvent. Poor resolution.
1.6	1 3 5	No Yes Yes	Not enough ablation. Good resolution, good image. No damage seen to the surface.

Example 6

Imaging Studies on KOR Laminated with D 50 Modified Slip and Print Test with the Imaged Plate

Imaging of D 50 modified slip on KOR was carried out using a xenon fluoride excimer laser lasing at 351 nm. Imaging of lettering was achieved using a CAD file. The following intensities and number of pulses were utilized:

Fluence J/cm^2	# of Pulses
1.5	8
2.0	6
3.1	4

The ablated/imaged plates were flood exposed under hot lamps for 5 1/2 minutes and washed in Solvit® for 6 minutes to give an image with 20-25 mils relief.

Microscopic examination confirmed that the image quality for all fluences was good, giving sharp profiles. However, the edges were rounded due to insufficient doses in those areas. There was no indication of surface thermal damage and the plate surface was smooth and even in all cases.

Example 7

Laser Ablation and Imaging on a Slip Modified with 4PHR D 50 and 4PHR 4-phenylazophenol (4-PAP)

In this Example, a mixture of UV absorbers was used with a slip film similar to that of Example 1. A casting solution for the modified slip was prepared using the following formulation:

Isopropanol	45.6 parts
Hexane	23.9 parts
VM&P Naphtha	21.6 parts
Macromelt 6900™	8.3 parts
Uvinul D 50	0.332 parts
4-phenylazophenol	0.332 parts

A film 5 to 7 mils thick was cast on a clear mylar backing sheet. Upon drying, the film had average thickness of 0.3-0.5 mils. The modified slip film was then laminated onto a KOR plate which was about 67 mils thick. Laser ablation and imaging was carried out as in Example 6. Once again, the image quality was excellent for all fluences.

Example 8

The printing plates of Examples 6 and 7 were tested for print quality on glossy paper using blue aqueous ink. The ink laydown was good. The letters printed were sharp and undistorted.

What is Claimed is:

1. A protective layer for a photocurable article comprising

a polymeric matrix and

a dopant having a high extinction coefficient in the range of 300-400 nm, the layer responding to a threshold dosage of radiation at a selected wavelength by photobleaching of the dopant and photoablation of the polymeric matrix.

2. The layer of Claim 1, wherein the dopant is 2,2'4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 4-phenylazophenol or mixtures thereof.

3. The layer of Claim 1, wherein the selected wavelength is 351 nm.

4. A photocurable article comprising

a photocurable composition having a low absorbance of radiation at a selected wavelength in the range of 300-400 nm and further comprising

an ~~initiator~~ activatable at the selected wavelength;

a protective layer comprising a polymeric matrix and a dopant having a high extinction coefficient in the range of 300-400 nm whereby said layer is photoablated by

a threshold exposure to radiation at the selected wavelength.

5. The photocurable article of Claim 4, wherein the dopant is 2,2'4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone or 4-phenylazophenol.

6. The photocurable article of Claim 4, wherein the selected wavelength is 351 nm.

7. The photocurable article of Claim 4, wherein the polymeric matrix is selected from the group comprising polyacetals, polyacrylics, polyamides, polyimides, cellulosic polymers, polybutylenes, polycarbonates, polyesters, polyethylene, polyphenylene ethers, and polyphenylene oxides.

8. The photocurable article of Claim 4, wherein the photocurable composition comprises a photopolymer selected from the group consisting of polyurethanes, including acrylate polyurethanes, acid-modified acrylate polyurethanes, amine-modified polyurethanes, rubbers, including acrylonitrile rubbers, and di- and triblock copolymers such as those made from styrene-isoprene and styrene-butadiene.

9. The photocurable article of Claim 8, wherein the photocurable composition comprises a photopolymer which is an amine-modified acrylate polyurethane or styrene-isoprene di- or triblock copolymer, or acrylonitrile rubber.

10. A method of making a laser imaged printing plate, the steps comprising

modifying a solid, uncured printing plate with a UV absorber;

ablating the UV absorber using a laser, thereby providing ablated and unablated areas;

exposing the printing plate to UV light, thereby curing the plate in the ablated areas;

developing the plate.

11. The method of Claim 10, wherein the UV absorber comprises

a polymeric matrix and

a dopant having a high extinction coefficient in the spectral output range of the UV light, the layer responding to a threshold dosage of radiation at a selected wavelength by photobleaching of the dopant and photoablation of the polymeric matrix.

12. The method of Claim 11, wherein the dopant is 2,2'4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 4-phenylazophenol or mixtures thereof.

13. The method of Claim 10, wherein the selected wavelength is 350-370 nm.

14. The method of Claim 13, wherein the selected wavelength is 351 nm.

15. The method of Claim 10, wherein the spectral output range of the UV light is 300-400 nm.

restricted

EXHIBIT B

PENDING CLAIMS AS OF MAY 13, 2002

10. A photosensitive element comprising:

- a backing layer;
- at least one layer of photopolymerizable material on said backing layer;
- at least one ablation layer which is ablatable by infrared radiation and opaque to non-infrared actinic radiation, wherein the infrared ablation layer is in direct contact with the at least one photopolymerizable layer and has a surface opposite the photopolymerizable layer capable of being exposed to laser ablation, the infrared ablation layer comprising:
  - at least one infrared absorbing material; and
  - at least one binder that is a polyacetal, polyacrylic, polyimide, polybutylene, polycarbonate, polyester, polyethylene, polyphenylene ether, or polyethylene oxide;

wherein the ablation layer is ablatable from the surface of the photopolymerizable layer upon exposure to infrared laser radiation.

11. The element of claim 10 wherein said backing layer is transparent.

12. The element of claim 10 wherein said photopolymerizable layer includes a polyurethane, acrylonitrile rubber, or a diblock or triblock copolymer made from styrene-isoprene or styrene-butadiene.

13. The element of claim 12 wherein said polyurethane is an acid-modified acrylate polyurethane or an amine-modified acrylate polyurethane.

14. The element of claim 10 wherein said infrared absorbing material absorbs infrared radiation having a wavelength of 10.6 μm.

15. CANCELLED

16. CANCELLED

17. The element of claim 10 wherein the infrared absorbing material is non-migratory.

18. The element of claim 10 wherein the infrared absorbing material constitutes about 1-20 weight parts per hundred of said ablation layer.